Oil Sheen Formation and Fate in an Open Sea Environment

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by

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ABSTRACT

Sea surface oil sheen samples were collected in the vicinity of an offshore oil production platform located on the Grand Banks of Newfoundland, Canada during an oceanographic expedition to assess the potential environmental impacts of production water discharges. Detailed chemical analyses showed oil droplets within the discharge stream from the production platform to be the source of petroleum hydrocarbons within surface-oil sheen samples. To improve our understanding of sheen production from the release of produced water discharges, a number of experiments were conducted in a meso-scale wave tank capable of simulating sea-state conditions. A high pressure subsurface release of crude oil was used to generate surface sheens, which were largely formed following the ascent of large (>100 µm) oil droplets. The oil associated with the droplets was found to be physically weathered prior to the formation of surface sheens. A biodegradation study conducted using sheen samples collected from the wave tank found that >80% of the hydrocarbons had been degraded over a 28 day period.

RÉSUMÉ

Des échantillons de lustre huileux ont été prélevés à la surface de la mer à proximité d'une plateforme de production de pétrole en haute mer située sur les Grands Bancs de Terre-Neuve, au Canada, lors d'une expédition océanographique qui visait à évaluer les répercussions possibles des rejets d'eau de production sur l'environnement. Les analyses chimiques détaillées ont montré que les hydrocarbures pétroliers présents dans les échantillons de lustre huileux à la surface de la mer provenaient de gouttelettes de pétrole présentes dans le courant d'évacuation de la plateforme de production. Afin d'améliorer notre compréhension de la production du lustre par le rejet de l'eau produite, un certain nombre d'expériences ont été menées dans une cuve à houle à méso-échelle pouvant simuler les conditions de mer. Un déversement de pétrole brut à haute pression sous la surface a permis de générer un lustre à la surface qui a été en grande partie formé à la suite de l'ascension de gouttelettes de pétrole de grande taille (plus de 100 µm). Le pétrole associé aux gouttelettes a été jugé altéré physiquement avant la formation du lustre en surface. Une étude de biodégradation menée sur des échantillons de lustre prélevés dans la cuve à houle a révélé que plus de 80 % des hydrocarbures avaient été dégradés après une période de 28 jours.

1 INTRODUCTION

Oil on the surface of water tends to spread and eventually form a very thin film or 'sheen.' Sheens can range in colour from rainbow to silver-grey depending on their thickness, which is usually less than 10 µm (Daling et al 1999). Potential sources of oil sheens in the marine environment include discharge from vessels, runoff, natural seeps, accidental spills at the surface and subsurface and operational discharges from oil and gas activities (National Research Council 1985, 2003). They are frequently difficult to find and collect in the open ocean, because they are very thin, usually less than 2-3 µm (Fraser et al. 2006). The presence of oil sheens has been observed in calm sea-states around offshore oil and gas platforms in Atlantic Canada (ERIN Consulting Ltd. & OCL Services Ltd. 2003).

Offshore oil and gas activities generate thousands of liters of production water daily, most of which is discharged into the ocean (Veil et al. 2004). Petroleum hydrocarbons represent a significant fraction of the chemicals of environmental concern in production water (Yeung et al. 2011). The formation of sea surface oil sheens and their relationship to production water discharges are not well understood. In Canada, the Offshore Waste Disposal Guidelines permit the discharge of <30 mg/L of oil in produced water based on a 30-day volume weighted average, or <44 mg/L based on an average oil-in-water concentration calculated twice over 24 hours (Canada-Newfoundland and Labrador Offshore Petroleum Board 2010). Production water contains oil in the form of 1) dispersed oil droplets suspended in the aqueous phase; 2) dissolved (i.e. soluble) components in the aqueous phase; and 3) free "bulk" oil that is separate from the aqueous phase (Fraser et al. 2006). Sheens are believed to be primarily associated with oil droplets (>100 µm) which are large enough to ascend without natural dispersion and small enough to avoid break up by natural turbulence (Erin Consulting Ltd. 2003, Lunel 1995).

Oil released into the environment undergoes a series of weathering processes, including evaporation of low molecular weight fractions, spreading of the oil, dissolution of water soluble components, photo-chemical oxidation, and biodegradation, all of which alter its physico-chemical characteristics and environmental fate (Harayama et al. 1999). These natural processes acting on the oil make it difficult for standard field methods and instruments (UV fluorescence) to determine the origin of oil discharged into the marine environment (Yang 2011). Since oil sheens in the open ocean have not been well studied, their formation from a subsea oil release, such as a produced water discharge, and their fate in the marine environment are not well understood (Fraser et al. 2006).

A review of the scientific literature revealed two critical disparities that need to be addressed: 1) understanding the process of sheen formation from oil droplets released during produced water discharges and 2) the fate of oil sheens in the natural environment. To address these issues, an oceanographic research expedition was conducted in July of 2011 to collect sheen and production water samples near the Sea Rose Floating Production Storage and Offloading (FPSO) unit located on the Grand

Banks of Newfoundland. In addition, a sample of crude oil from the facility was acquired for detailed chemical analyses. Fresh produced water samples from the discharge stream were examined using a Laser *In-situ* Scattering and Transmissometry (LISST-100x) instrument to determine suspended particle size distribution. The sheen samples, produced water, and crude oil were evaluated using a variety of analytical chemistry techniques and compositional indices, including carbon preference index (CPI), and pristine/C_{17} and phytane/C_{18}, to help determine the hydrocarbon origin of the sheens.

A mesocosm-scale wave tank at the Bedford Institute of Oceanography was used to conduct a number of controlled experiments simulating natural sea-state and environmental conditions to evaluate oil droplet size distribution and potential sheen formation following a subsurface injection of oil droplets simulating a produced water discharge. From the experiments, the fate of petroleum hydrocarbons within the resulting oil sheens was determined by detailed time-series chemical analyses.

2 MATERIALS AND METHODS

2.1 CHEMICALS AND REAGENTS

The crude oil and produced water samples were provided by the Sea Rose Floating Production Storage and Offloading (FPSO) vessel. All individual polycyclic aromatic hydrocarbons and alkane standards were purchased from Absolute Standard Inc. (Connecticut, USA). Deuterated standards, used for checking method recoveries, are as follows: d_{10}-phenanthrene, d_{10}-pyrene, d_{12}-benzo[*a*]pyrene, d_{12}-benzo[*b*]fluoranthene, d_{14}-dibenz[*a*,*h*]anthracene; dueterated alkanes d_{26}-dodecane, d_{36}-heptadecane, d_{50}-*n*-tetracosane, d_{66}-*n*-dotricontane, and 5β-Cholestane (Cambridge Isotope Laboratories, Inc. Canada). Samples for chemical analysis were extracted with dichloromethane (pesticide grade distilled in glass, Caledon, Georgetown, Ontario, Canada).

2.2 SAMPLE COLLECTION AND IN-SITU MEASUREMENTS

Oil sheen samples were collected within the 5 km exclusion zone around the Sea Rose FPSO with the support of the Canadian Coast Guard oceanographic research vessel, *Hudson*, in July of 2011. A Hydro-Bios (Hydro-Bios Apparatebau GmbH, Germany) surface sampler (Guitart et al. 2008) was deployed by hand from a Zodiac for the collection of sheen samples. Collection was done from the surface to a depth of 1 cm (surface microlayer). Fresh produced water samples treated to acceptable regulatory compliance for ocean discharge were drawn into 2.3 L amber glass bottles by technicians on the FPSO for time-series particle size distribution (PSD) analysis (PSD: 2.5 – 500 µm) using a Laser In-situ Scattering and Transmissometry (LISST-100x, Sequioa, USA) particle counter at 12, 30, 56, 125 and 192 hrs after collection. A total of 100 individual readings were acquired at each time point, for each raw produced water sample introduced into a LISST optical chamber fitted with a magnetic stir bar.

Background readings for the LISST were established prior to the analysis with 0.22 µm filtered seawater.

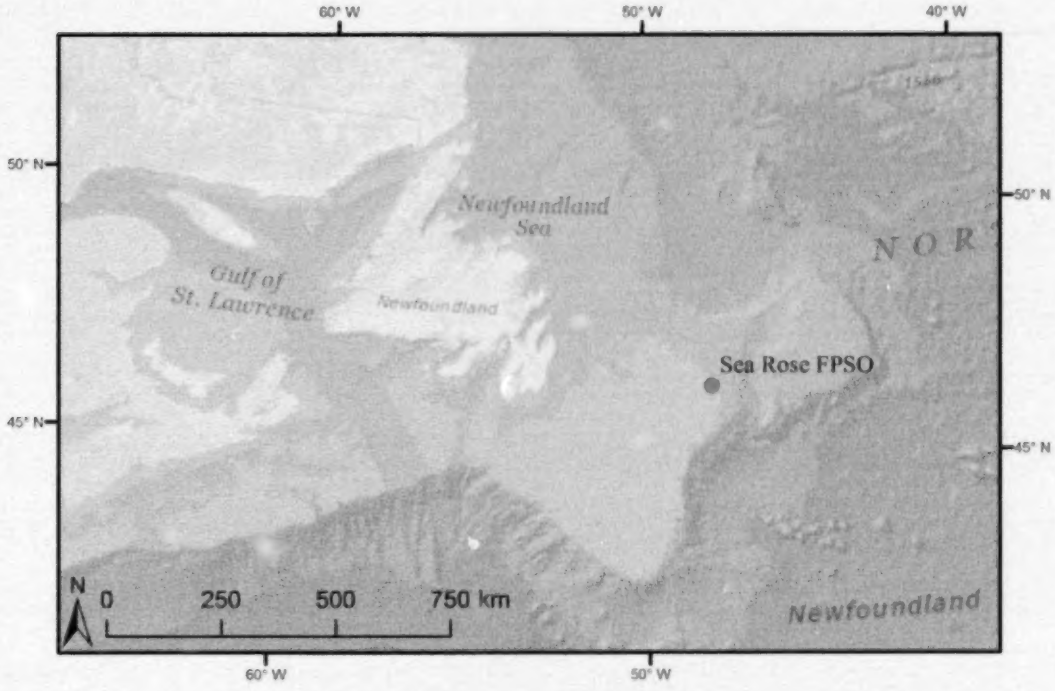

Figure 1 Location of the Sea Rose FPSO on the Grand Banks

2.3 LAB ANALYSES OF PROCURED SAMPLES

2.3.1 Oil characterization

A sample of Sea Rose crude oil was used for physical measurements of viscosity (Brookfield LVT; UL Enhanced Adapter; calibrated reference oil IFO 40) and density (Mettler Toledo DM45; calibrated standard lot# 171312) The chemical composition of this unweathered oil was evaluated for SARA (saturates-aromatics-resins-asphaltenes) using thin-layer chromatography coupled with scanning flame ionization detection (TLC-FID) with an Iatroscan MK-6 (Maki and Saki 1997). Detailed chemical analysis of this oil's constituents was accomplished using gas chromatography with flame ionization detection (GC-FID) and gas chromatography coupled to mass spectrometry (GC-MS).

2.3.2 Extraction and analyses

Oil sheens were extracted from the surface microlayer samples according to methods in Cole et al. (2007). For the purpose of this study, the sheen sample extracts were

compared to a "reference standard" prepared from Sea Rose crude oil using gas chromatography with flame ionization detection and subsequently the extracts were analyzed for saturates, aromatics, resins and asphaltenes (SARAs) by TLC-FID. Most of the evaluations were for qualitative purposes to help identify the hydrocarbon source associated with sheen formation.

Following the method of King and Lee (2004), the sheen extracts were further analyzed using high resolution gas chromatography (Agilent 6890 GC) coupled to a mass selective detector (Agilent 5973N) (Willmington, DE, USA) operated in the selective ion monitoring mode (SIM) using the following GC conditions: MDN-5S column (30 m x 0.25 mm id with 0.25 µm film thickness, Supelco Canada), cool on-column injection with oven track mode (track 3°C higher that the oven temperature program), 80°C hold for 2 min, ramp at 4°C/min to 280°C, hold for 10 min. Quantification criteria for PAH included retention time matching, i.e. within ±0.010 min of the retention time of the certified standard and comparing the relative abundance of the qualifying ion(s) (±10%), the molecular ion, and one or more qualifier ions in the mass spectrum of the compound with the commercial standard.

Average ± standard deviation of added recovery standards for all samples extracted and processed by GC-MS (Appendix) were: d10-phenanthrene (80.2 ± 3.0%), d10-pyrene(82.3 ± 3.0%), d12-benzo[a]pyrene (91.1 ± 5.0%), d12-benzo[b]fluoranthene (87.3 ± 5.5%), d14-dibenz[a,h]anthracene (90.8 ± 10.7%); deuterated alkanes d26-dodecane (70.8 ± 4.5%), d36-heptadecane (80.4 ± 3.4%), d50-n-tetracosane (96.8 ± 3.4%), d66-n-dotricontane (96.2 ± 7.4%), and 5β-Cholestane (84.2 ± 4.5%).

Using a modified version of US EPA method 3510 C (1996), raw produced water was extracted three times with 50 mL portions of dichloromethane using a separatory funnel, and all extracts were combined. The bulk of the solvent was removed using a Turbo Vap II concentrator (Zymark, USA). A second sample of produced water was purged with nitrogen for 24 hr to represent a sample that had undergone natural weathering. After purging, the sample was extracted similar to the fresh produced water sample. The produced water extracts were analyzed using the same analytical techniques that were used for the sheen samples.

2.4 WAVE TANK STUDIES

The wave tank facility is located at the Bedford Institute of Oceanography (BIO). The tank dimensions are 2 m high, 0.6 m wide, and 32 m long (Figure 2). The facility is capable of producing regular non-breaking and breaking waves and it is equipped with a flow-through system to simulate natural sea currents at a velocity of 0.4 cm/s (King et al. 2013; Li et al. 2009). For this study, the wave tank was operated in flow-through mode under non-breaking wave conditions, because under breaking waves the sheens would not remain intact, but instead they would be dispersed into the subsurface water column.

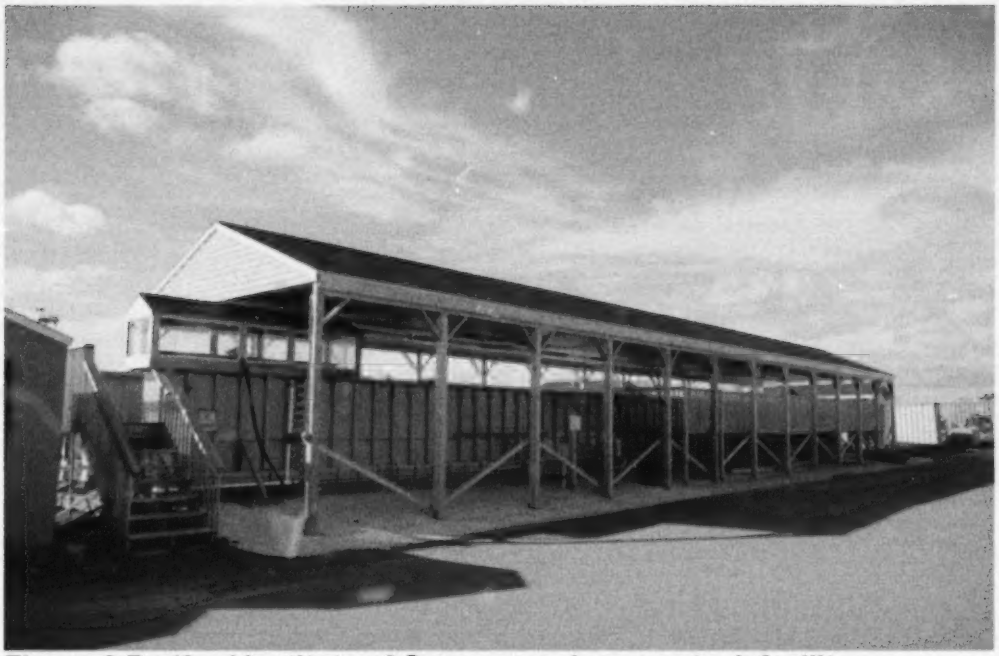

Figure 2 Bedford Institute of Oceanography wave tank facility

A number of wave tank runs were conducted to aid our understanding of how sheens are formed from a sub-sea oil release, and to evaluate their fate under realistic sea state conditions. During the experiments, fresh (un-weathered) oil was discharged under pressure (40 psi, 4.8 L/min) through a conical nozzle (2.4 mm orifice) at depth of 1.5 m. Figure 3 demonstrates the location of in-situ equipment, sampling position and the subsurface release of oil. A LISST was situated 1 m downstream from the oil release at a depth of 75 cm. Using the Hydro-Bios sampler, sheen samples were collected from the surface where the first oil droplets had risen, and sampling continued at this location for the following time points: 5, 15, 30, and 60 minutes. A background sample of the sea water was taken prior to the oil release.

A subsample (20 mL) of all collected sheen samples was used to measure interfacial tension in a temperature controlled environment (20.7 ± 0.4°C) following the Wilhelmy plate method (Drelich et al. 2002). The remaining sheen samples were then processed using the same analytical techniques described previously for sheen and produced water field samples.

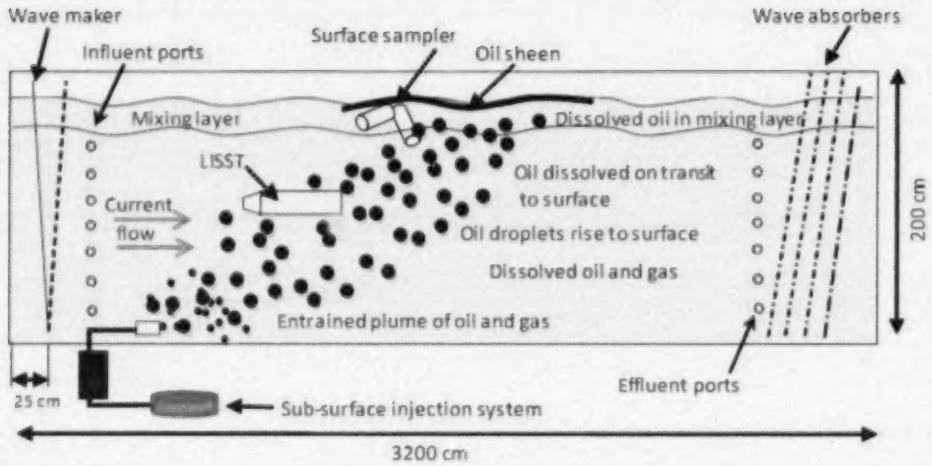

Figure 3 Wave tank sub-surface oil release (not to scale) displaying large oil droplets that ascend to the surface to form sheens

2.5 BIODEGRADATION OF OIL SHEENS IN THE WAVE TANK

2.5.1 Bushnell-Haas broth preparation

Bushnell Haas broth (Difco, Becton, Dickinson and Company), which contains nitrate and other trace elements, was prepared by dissolving 3.27 g of the dry powder in 1.00 L of deionized distilled water. The broth was boiled and autoclaved according to the manufacturer's instructions. Bushnell-Haas broth was added to each flask to help sustain extended microbial activity in this closed system and prevent the biodegradation process from becoming nutrient limited (Latha and Kalaivani 2012).

2.5.2 Experimental microcosm set-up

The procedures of Campo et al. (2013) were followed to prepare the microcosms. To avoid contamination, equipment and materials were autoclaved and sterile-sealed prior to use. Since microbial populations change upon storage, the experiments commenced immediately after surface sheen samples were collected from the wave tank. Sheen samples were collected at 30 minutes into operations to ensure a sufficient quantity of material, and because previous sheen work showed that all chemical groups (e.g., alkanes, M-PAHs and PAHs) are present by this time.

Microcosms were prepared in triplicate 150 mL Wheaton trypsinizing flasks with a Teflon lined screw cap, each containing 100 mL of the wave tank sheen sample and 2 mL Bushnell-Haas medium.

One triplicate set of microcosms was immediately sacrificed (at t = 0) by adding 10 mL dichloromethane (DCM). All remaining microcosms were placed on an orbital shaker (MaxQ 2000, Fisher Scientific) and mixed at 200 rpm, incubated at a seawater temperature of 15 ± 0.5 °C and sacrificed at time points 2, 7, 15 and 28 days. Microcosm samples were extracted and analyzed by GC-MS, using the procedures previously mentioned.

3 RESULTS AND DISCUSSION

3.1 PHYSICAL MEASUREMENTS OF CRUDE OIL

All physical measurements were recorded at 15°C, which is a standard temperature for most oil measurements permitting the comparison of similar petroleum products. The crude oil viscosity was 16.3 cS and its density was determined to be 0.856 g/cm^3. An API gravity of >31 classifies it as a light grade crude oil. A sample of fresh Sea Rose crude oil was weathered by sparging with nitrogen until its mass was reduced by 15%. This weathered Sea Rose crude was used to compare with the chemical composition of the collected sheens. It would have been useful to see how the physical parameters of this weathered oil compared with the sheens, but there was insufficient quantity of sheen sample on which to conduct physical measurements.

3.2 ANALYSES OF OIL SHEENS, PRODUCTION WATER AND CRUDE OIL

Analysis of freshly collected, raw, produced water revealed suspended particles that covered the entire size range measured by the LISST from 2.5 to 500 µm (Figure 4). Over time, the concentration of large particles decreased and by 96 hours, the large particles were no longer detectable and only small particles were present. Although some large particles were detected in the fresh produced water, there are a couple of important factors to consider. First, the LISST cannot distinguish between oil droplets and other particles present in produced water (e.g. precipitated metal salts arising from sample exposure to oxygen) or the metal precipitates that adhere to oil droplets (Azetsu-Scott et al. 2007). Second, the length of time required to take an initial measurement may have been too long to capture large oil droplets (assuming a large oil droplet would quickly rise in the 2.3 L amber glass bottle used to collect the fresh produced water). As a result of these two factors we were unable to conclude if large oil droplets were present. However, Azetsu-Scott et al. (2007), using UV epi-fluorescence microscopy, have identified buoyant aggregates of oil droplets and inorganic metals in produced water that rise to the sea surface.

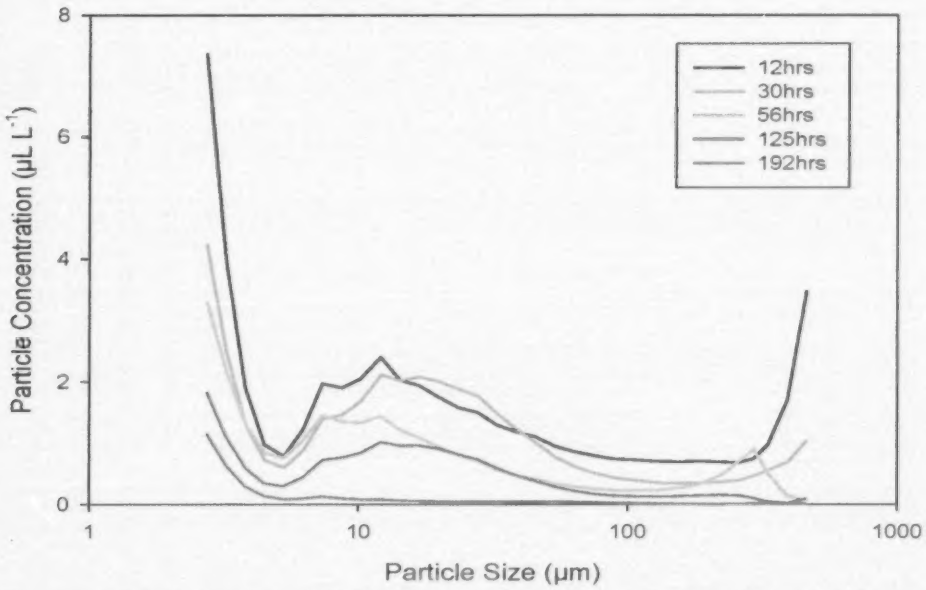

Figure 4 Particle size distributions of raw produced water at different times

The raw produced water extracts generated TLC-FID chromatograms characteristic of Sea Rose crude oil (Figure 5). Some sheen samples (SN1, SN6, SN7 and SN8) had detectable levels of only high molecular weight hydrocarbons (resins and asphaltenes). Others (SN2, SN3, SN4, and SN5) had detectable levels of saturates, aromatics, resins and asphaltenes (SARAs), requiring further evaluation using additional analytical techniques.

Samples containing detectable levels of SARAs, along with crude oil and production water extracts were analysed by GC-FID. GC-FID chromatograms of two sheen samples (SN3 and SN5) illustrated patterns consistent with the weathered produced water extract (Figure 6). As a result of these findings, all of the sheen samples were further evaluated using GC-MS.

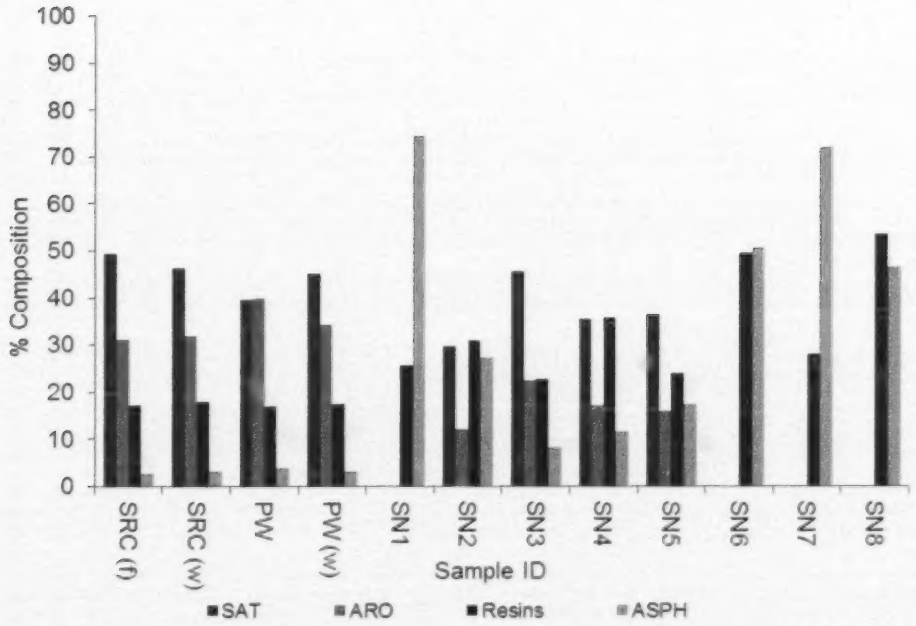

Figure 5 TLC-FID %SARAs (saturates, aromatics, resins, asphaltines) detected in Sea Rose crude (SRC), f = fresh, w = weathered, production water (PW), and sheen samples (SN); numbers indicate experimental trial

GC-MS profiles of the sheen and production water samples were used to authenticate the hydrocarbons detected by TLC-FID and GC-FID. Sheens SN6, SN7 and SN8 had non-detectable levels (<100 ppb) of hydrocarbons (Figure 7). The remaining sheen samples contained detectable levels of saturates and aromatics, mostly methylated-PAHs (M-PAHs). These findings indicate that all the field collected sheen samples, regardless of how they were formed, have been weathered to some extent.

Detailed chemical analysis revealed that the more complex organic compounds, such as the PAHs and M-PAHs, were present in low concentrations or they were non-detectable. Based on these results, it appears that changes in oil composition were the result of the natural weathering rather than biodegradation, which would have involved first the degradation of single bonded compounds such as the saturates, followed by more complex compounds containing double bonds, such as aromatics (Olson et al. 1999).

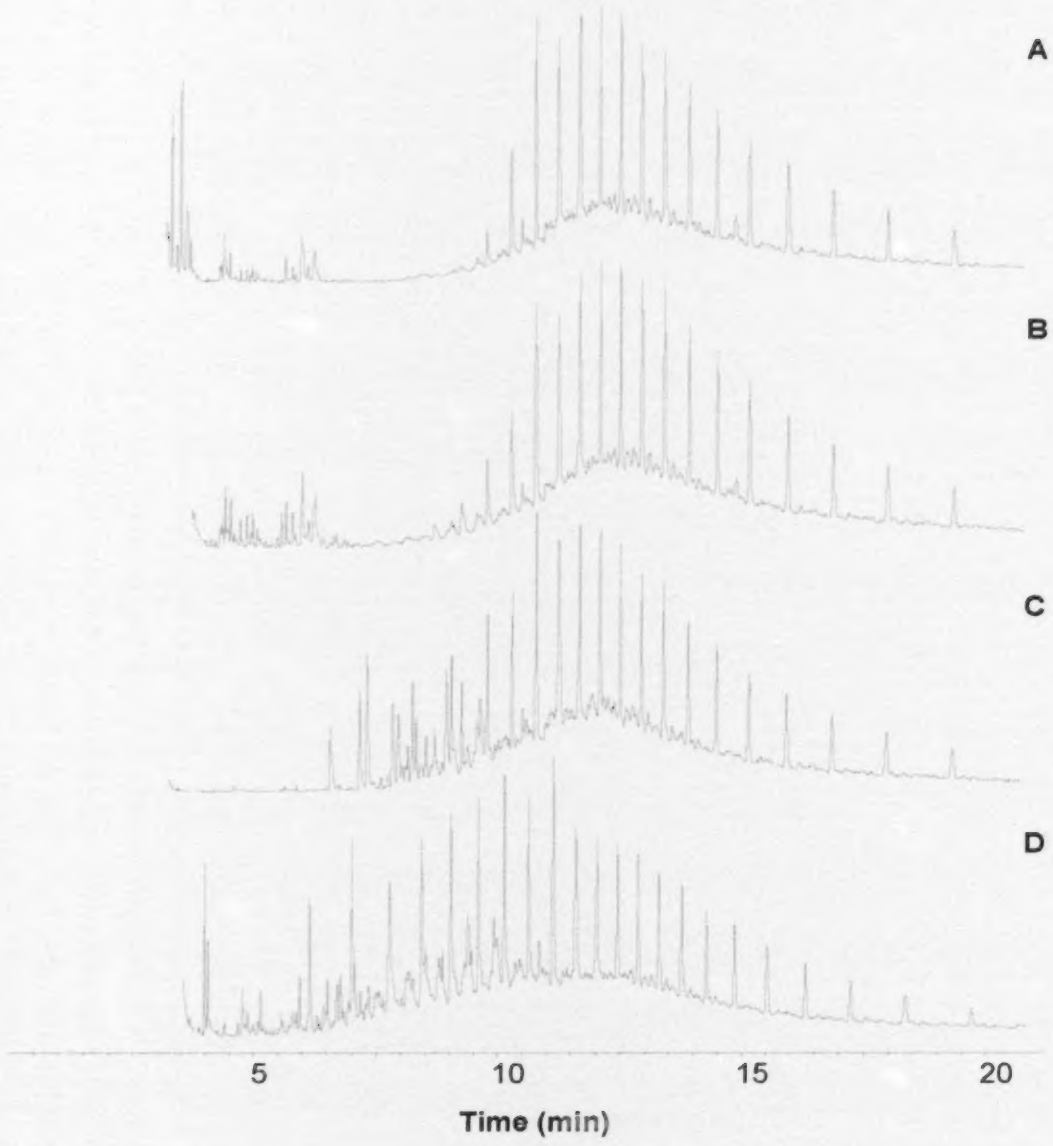

Figure 6 GC-FID chromatograms of A) surficial sheen sample SN3, B) surficial sheen sample SN5, C) artificially weathered production water extract, and D) artificially weathered Sea Rose crude oil

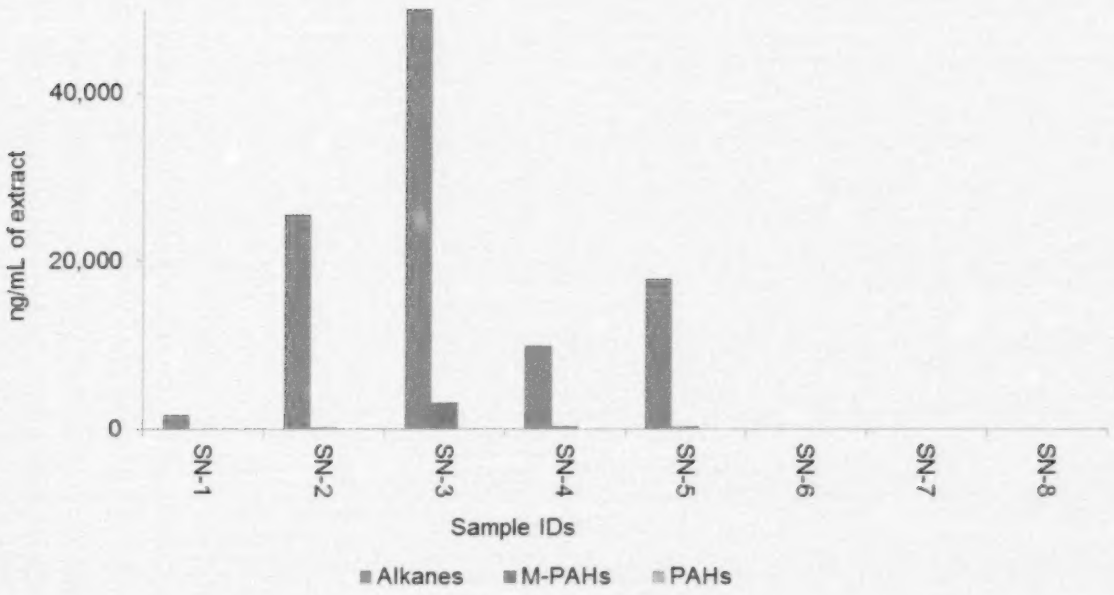

Figure 7 Saturates, alkyl-PAHs and PAHs detected in sheens collected near an offshore oil and gas platform in Atlantic Canada

3.2.1 Alkanes in crude oil, production water and sheens

In this study, samples of crude oil and production water were obtained to determine the source of oil that produced the sheens collected near the Sea Rose FPSO. The measurement of individual alkanes permits the determination of the carbon preference index (CPI), which provides supportive evidence for relative incorporation of various alkane sources (Ekpo et al. 2012). CPI values range from 0.9 to 1.39 for various anthropogenic sources (Zakaria et al. 2000), and values above these are most likely of biogenic origin. The CPI was calculated using the following formula (1):

$$\mathrm{CPI} = \frac{1}{2}\left[\frac{\sum nC_{17} - nC_{31}}{\sum nC_{16} - nC_{30}} + \frac{\sum nC_{17} - nC_{31}}{\sum nC_{16} - nC_{30}}\right] \qquad (1)$$

where *C* represents the concentration of *n*-alkane containing specific carbon numbers.

In addition to CPI values, pristane/C_{17} and phytane/C_{18} ratios are usually unaltered within the first 8 days of weathering and they can be used to identify the source of light crude oils (Qimin et al. 2007), such as the Sea Rose crude oil. Pristane and phytane are branched alkanes that are ubiquitous in most crude oils, making them useful as biomarkers for evaluating the extent of biodegradation (Okoro 2010). However, caution must be exercised, since some microbes will break down these more persistent

branched alkanes. The CPI, pristine/C_{17} and phytane/C_{18} ratios are illustrated in Figure 8 for weathered crude oil, weathered production water and sheen samples collected near the Sea Rose FPSO.

N-alkanes were non-detectable in sheen samples SN6, SN7 and SN8. There were no detectable levels of C_{17} to generate a pristine/C_{17} ratio for SN1 and SN4, making it difficult to determine the origin of the oil detected in these samples. SN3 and SN5 more closely match the Sea Rose weathered produced water, although there is variability in the CPI, pristine/C_{17} and phytane/C_{18} ratios. However, using an analysis of variance gave *p*-values (0.99) >0.05 indicating that the weathered crude oil, production water, SN2, SN3, and SN5 were statistically of the same origin. This statistical evidence suggests that the sparse sheens collected near Sea Rose came from production water discharge. Knowing the formation, fate and transport of these thin surficial oil layers on seawater is essential to understanding their impacts on the marine environment, which led to further studies using the wave tank facility.

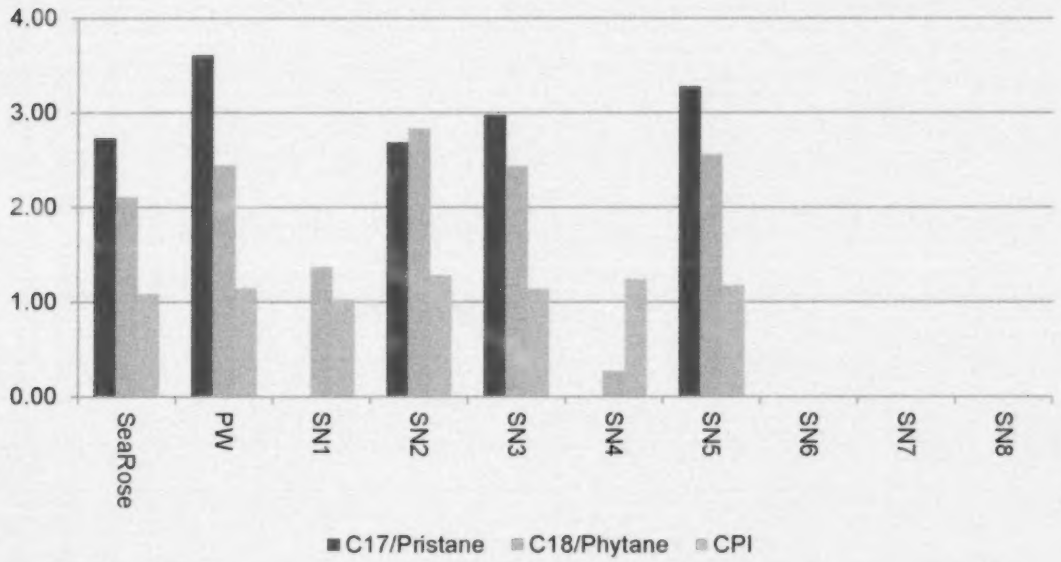

Figure 8 Comparison of CPI, pristine/C17 and phytane/C18 ratios of sheen samples to Sea Rose crude oil and production water

3.3 WAVE TANK STUDIES

Oil sheen generation from a subsurface release of oil in a wave tank was performed in duplicate to validate our findings from the field. Average sea water temperature and salinity for the duplicate trials were 14.0°C and 28.8 part-per-thousand (ppt) respectively.

The in-situ LISST data revealed that the bulk of the oil droplets ranged in size from 100 to 350 µm (Figure 9). These large oil droplets (>100 µm) ascended to the water surface to form very thin, iridescent sheens, with no noticeably thick oil slicks.

The averaged interfacial tension results (n = 2, Figure 9) revealed that in the initial stages of sheen formation, there is a drastic reduction in interfacial tension. The surface tension approaches seawater background levels at the 60 minute time point.

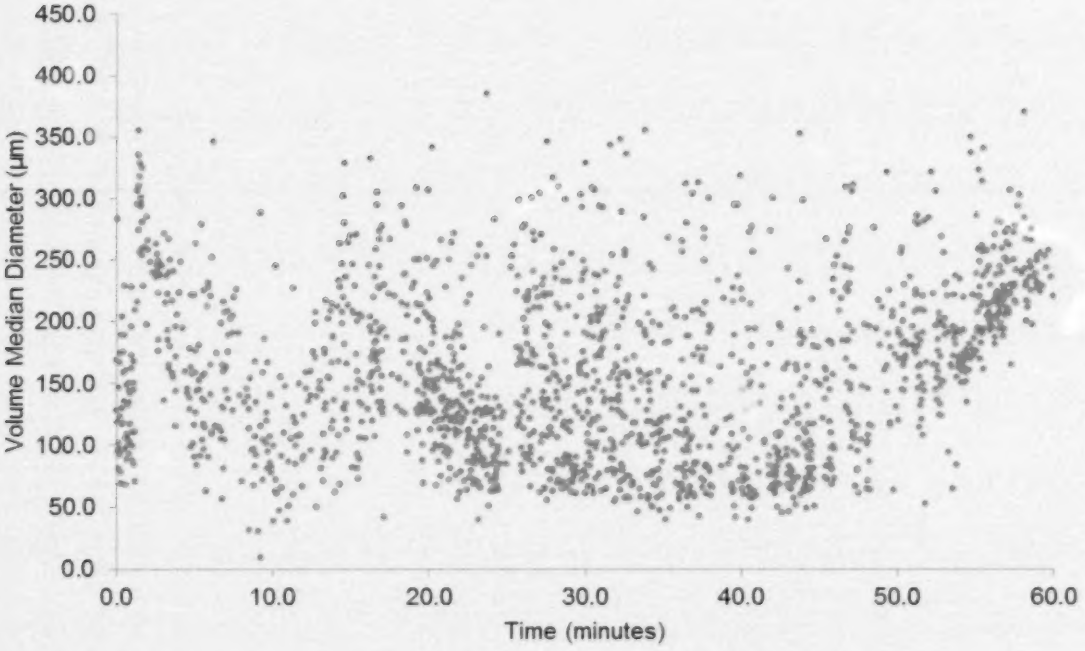

Figure 9 Oil droplet size distribution during a subsurface release of oil

TLC-FID data revealed that as sheens form in realistic sea conditions, their chemical composition is constantly changing with time due to physical modifications (Figure 11) including evaporation, spreading, dissolution and dilution. These changes were most notable at 60 minutes, by which time only saturates and resins were detectable in the sheens. In comparison with the other chemical groups, the asphaltenes were non-detectable, which was most likely due to dilution from current flow, since it was observed that the sheen concentration decreased dramatically with time.

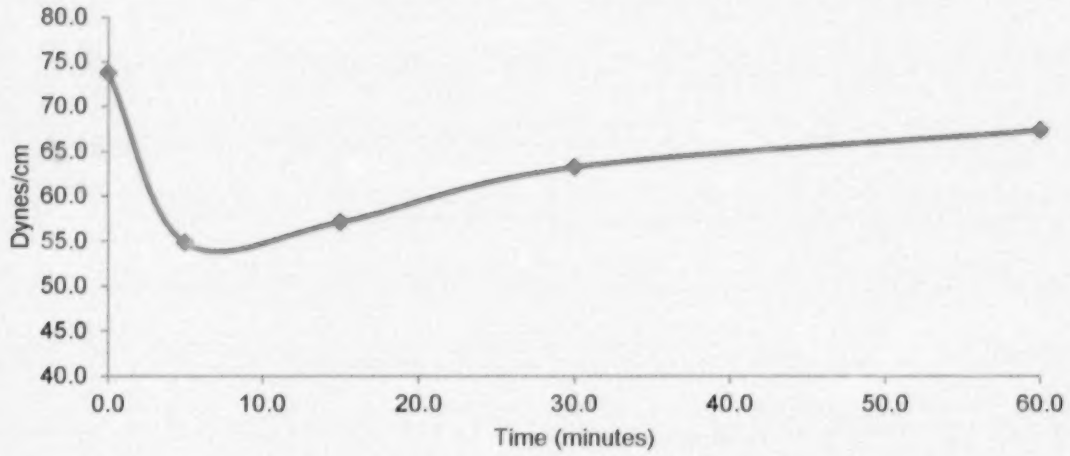

Figure 10 Changes in sea water surface tension (average, n=2) during oil sheen formation as physical modifications act on the sheen

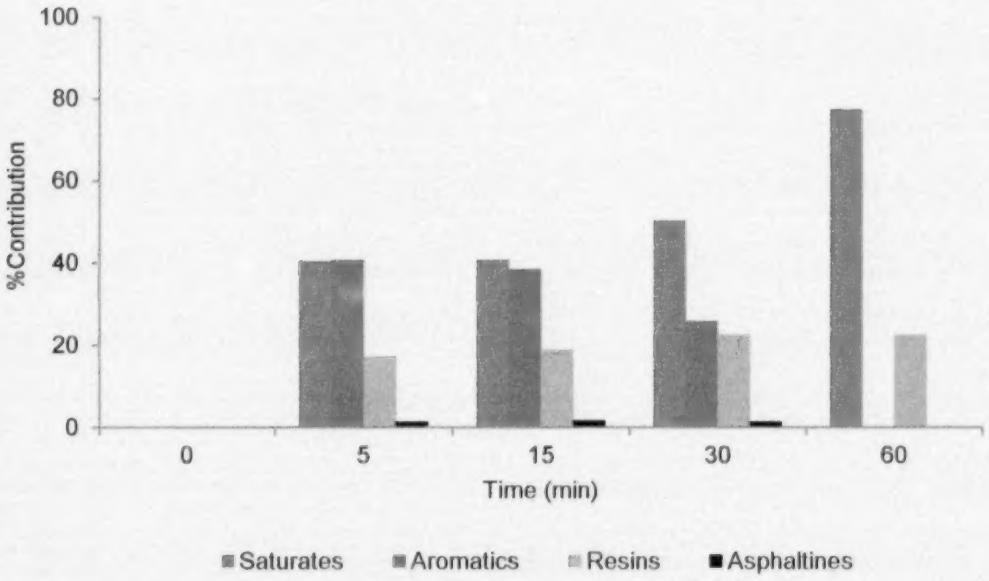

Figure 11 Averaged (n = 3) temporal chemical composition changes of oil sheens generated in the wave tank from a subsurface release of Sea Rose crude oil

Natural transformation of the sheen chemical composition was authenticated by GC-FID. After being released, the oil continuously decomposed, as large oil droplets ascended to the surface to form sheens (Figure 12). It was evident within the first five

minutes of sheen collection that most of the lighter hydrocarbons had been lost. The fate of sheens was characterized by a decline in carbon chains up to C_{17} within 60 minutes of wave tank operations.

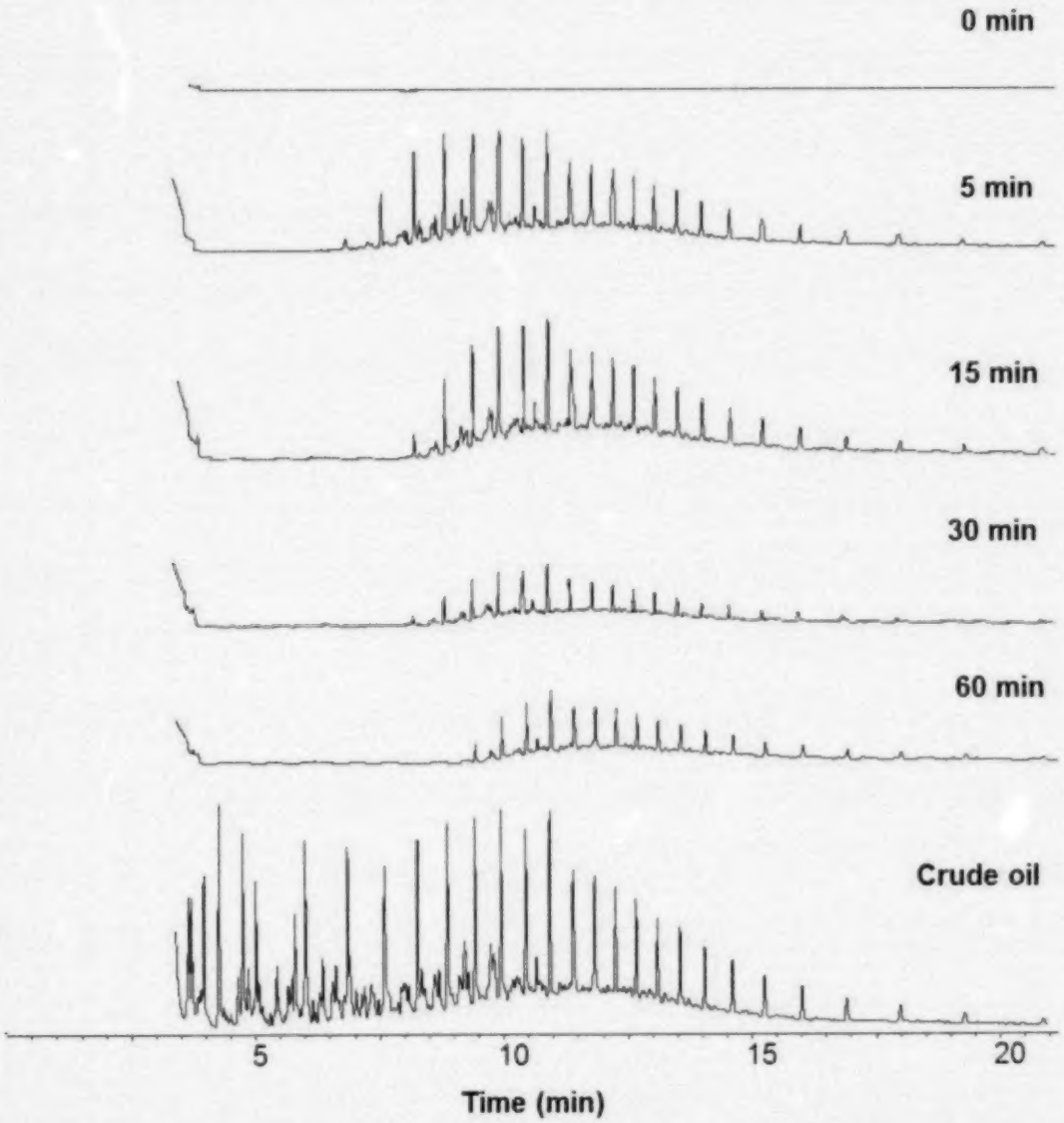

Figure 12 GC-FID chromatograms of the Sea Rose crude oil compared with wave tank surface water to examine sheens collected at 0 (oil not yet reached the surface), 5, 15, 30, and 60 min

3.3.1 GC-MS and compositional indices

GC-MS data demonstrated the temporal changes in saturates and aromatics in sheens collected at various time points during wave tank studies (Figure 13). The results showed that the concentration of oil components associated with sheens was rapidly changing in a physical environment where evaporation, dissolution, spreading and dilution were acting on the sheens.

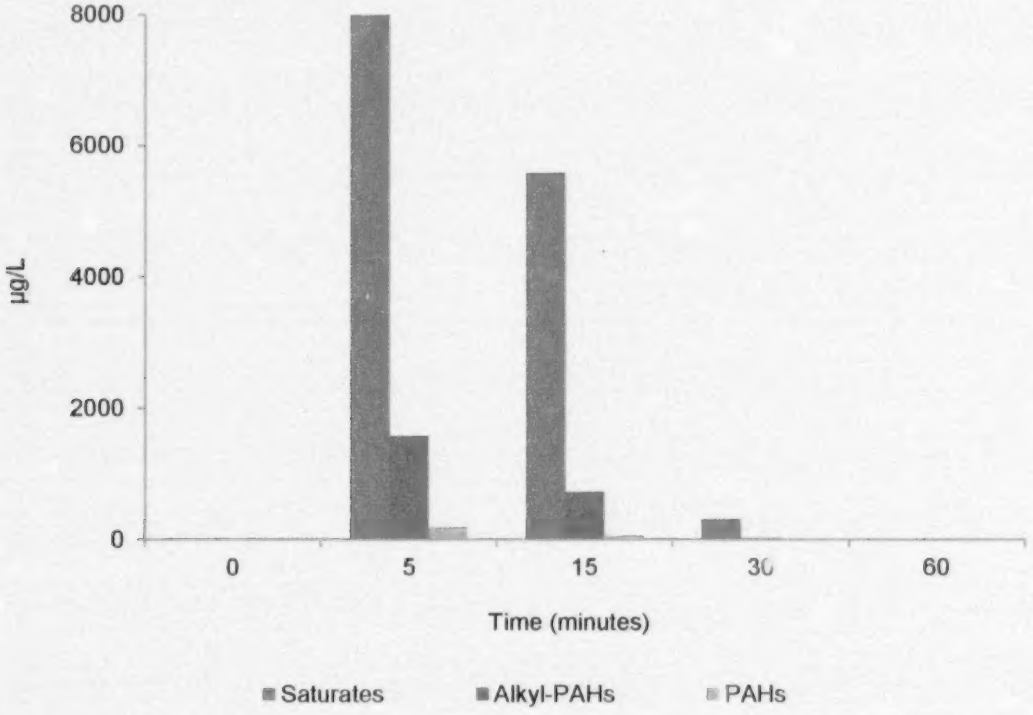

Figure 13 Temporal changes in the chemical composition of oil sheens (n = 3) formed in the wave tank facility

Similar to the field sheen samples, compositional indices were used to evaluate the fate of newly formed sheens in the wave tank. The CPI, pristine/C_{17} and phytane/C_{18} ratios illustrated that the chemical composition of the sheens varied considerably with time in a simulated sea environment (Figure 14). These results confirm the influence of the physical processes on the sheens, since microbial degradation is not expected to make a significant impact within a one hour experiment.

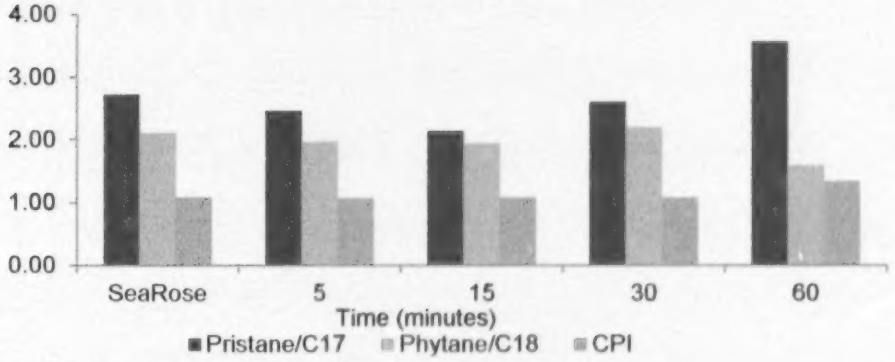

Figure 14 Comparison of CPI, pristine/C17 and phytane/C18 ratios of wave tank sheen samples (n = 3) to the original oil

3.3.2 Chemometric analysis and biodegradation of oil

17α(H), 21β(H)-hopane was used as a conservative biomarker to monitor the long-term fate of sheens and bioremediation effectiveness. Hopanes are large molecules that are resistant to microbial attack and they have been used to evaluate the biodegradation of petroleum hydrocarbons (Venosa et al. 1997). Figure 15 illustrates the hopane-normalized biodegradation of alkanes, M-PAH and PAHs with time. The error bars represent one standard deviation from the mean (n = 3). The results show that the majority of the chemical compounds are degraded by 28 days.

It is common to use a decay model to represent the biodegradation of oil; therefore, the rate law of the analyte (e.g., alkanes, PAHs, M-PAHs) is expressed as $\left(\frac{dC}{dt}\right)_t$, the rate law of hopane is expressed as $\left(\frac{dH}{dt}\right)_t$, and the biodegradation rate of the analyte $-kC$ is related by

$$\left(\frac{dC}{dt}\right)_t = \frac{C}{H}\left(\frac{dH}{dt}\right)_t = -kC \qquad (2)$$

where C is the concentration of analyte, H is the concentration of hopane, and k is the first-order biodegradation rate constant for the analyte.

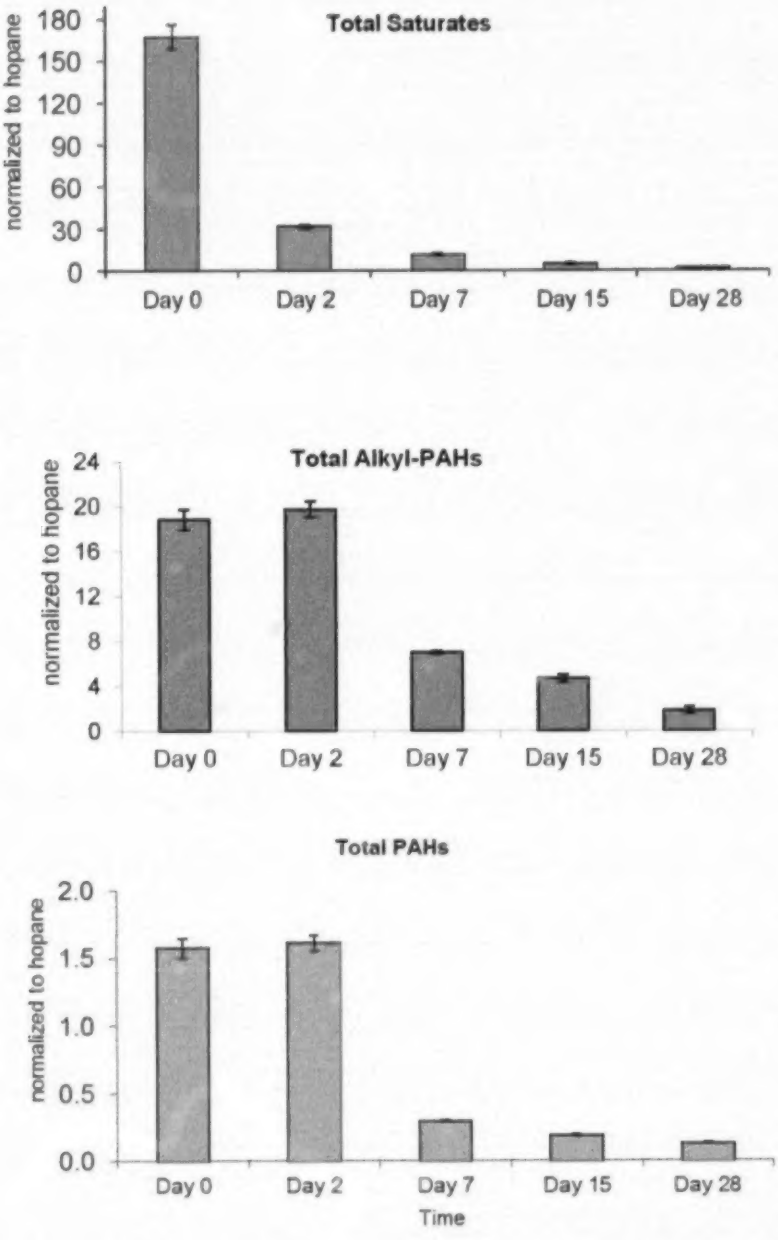

Figure 15 Hopane-normalized biodegradation of saturates, alkyl-PAHs and PAHs (n = 3)

Using the definition of the derivative of a quotient, equation 2 can be rewritten as

$$\frac{d\left(\frac{C}{H}\right)}{dt} = -k\left(\frac{C}{H}\right) \qquad (3)$$

Integrating equation 3 yields the first-order relationship

$$\left(\frac{C}{H}\right) = \left(\frac{C}{H}\right)_0 e^{-kt} \qquad (4)$$

where $\left(\frac{C}{H}\right)$ is the time-varying hopane-normalized concentration of an analyte, and $\left(\frac{C}{H}\right)_0$ is the value of that quantity at time zero. If the natural log is applied to both sides of equation 4 and it is rearranged to follow the format of a straight line, y = mx+b, it becomes

$$ln\left(\frac{C}{H}\right) = ln\left(\frac{C}{H}\right)_0 - kt \qquad (5)$$

where $ln\left(\frac{C}{H}\right)_0$ is the y-intercept and $-k$ is the slope of the line or the biodegradation rate constant and *t* represents time.

Figure 16 illustrates the first order linear plots of the hopane-normalized biodegradation of alkanes, M-PAHs and PAH over 28 days. The results show a rapid decline in chemicals associated with sheens. Regression analysis of the data from equation 5 for alkanes, PAHs and M-PAHs produced *p-values* <0.05 and r^2 values of 0.82, 0.78 and 0.95 respectively. The statistically significant linear results indicate that biodegradation was the main pathway for the decrease in hydrocarbon concentrations.

In addition, the half-life ($t_{\frac{1}{2}}$) can be determined by modifying equation (5) to produce

$$-kt\frac{1}{2} = ln\left(\frac{\left(\frac{C}{H}\right)_0 \div 2}{\left(\frac{C}{H}\right)_0}\right) = -ln2$$

$$t\frac{1}{2} = \frac{ln2}{k} \qquad (6)$$

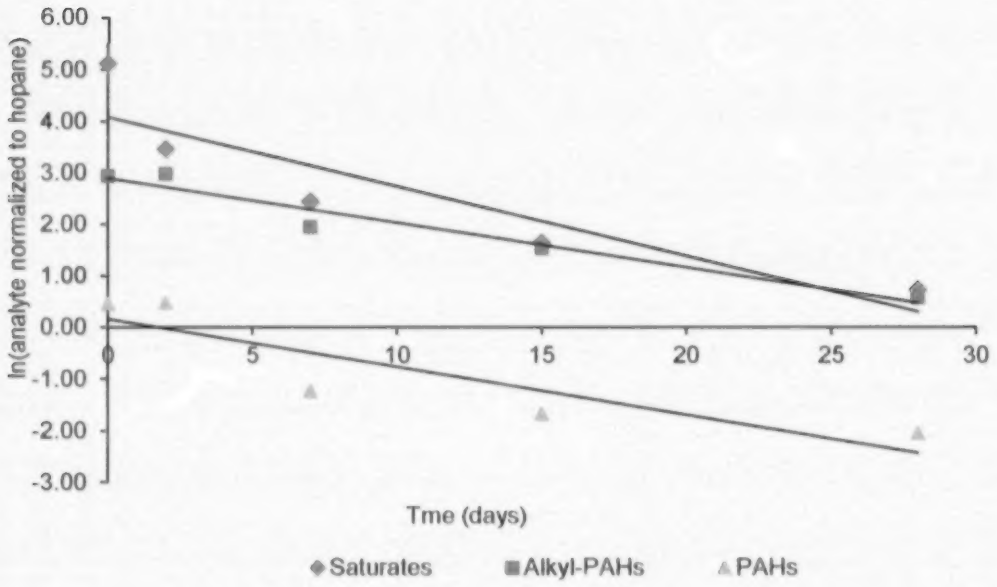

Figure 16 First order linear plots of the rate of decay for hopane-normalized saturates, alkyl-PAHs and PAHs

The half-life (the point where hydrocarbon concentrations have decreased by half) was calculated to be 5.1, 8.0 and 7.5 days for alkanes, M-PAHs and PAHs respectively. The results show that it takes less time to degrade the alkanes compared with the aromatics.

The main metric for evaluating effectiveness is the percent biodegradation (equation 7) through time of various analytes of interest (Bragg et al. 1994, Venosa et al. 1996):

$$Percent\ biodegradation = \left[1 - \frac{\left(\frac{C}{H}\right)_t}{\left(\frac{C}{H}\right)_0}\right] \times 100 \qquad (7)$$

The percent biodegradation of the sheens at 28 days was calculated to be 98.77 ± 0.02%, 90.54 ± 1.61% and 91.79 ± 0.59% for alkanes, M-PAHs and PAHs respectively. A greater percentage of the more concentrated alkanes compared with the aromatics were degraded at 28 days. Physical processes caused the initial loss of hydrocarbons from the sheens, but biodegradation was the determining factor in the long term.

4 CONCLUSIONS

The discharge of production water into the environment has the potential to release oil droplets large enough to rise to the sea surface and form oil sheens. On the basis of chemical analyses (e.g. TLC-FID, GC-FID and GC-MS) the field samples of sheens were statistically similar in saturate composition to Sea Rose crude oil and production water. Particle size and chemical analysis of produced water samples support the hypothesis that weathered oil droplets (>100 μm) contributed to the formation of the observed surface sheens.

This conclusion was also supported by the results of subsequent wave tank tests, which revealed that oil droplets were weathered by physical processes as they rose to the surface. Furthermore, the oil sheens associated with the light crude oil produced by the FPSO underwent natural weathering processes (e.g. dissolution, evaporation, photo-oxidation and biodegradation) that rapidly altered their chemical composition. Within 28 days, >90% of the measured hydrocarbons in the sheens were biodegraded. Through biological processes, it was evident that the saturated hydrocarbons degraded faster compared with the more complex aromatics (containing fewer carbons, which are arranged in double bonds). Therefore, under similar environmental conditions, the impact of sporadic sheens on the marine environment can be considered short-term, since natural physical and biological processes acting on the sheens rapidly change their chemical composition and decrease their concentration within hours to days. The open sea environment is uncontrolled making it difficult to determine when sheens are formed and environmental conditions acting on the sheens can make it challenging to verify the source of sheen formation. However, by conducting controlled, subsurface oil release experiments in a wave tank, it was possible to study the formation, transport, and fate of sheens resulting from produced water discharges in the open sea.

5 ACKNOWLEDGEMENTS

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7 APPENDIX

GC-MS data for crude oil, produced water, field collected sheens and sheens generated in the wave tank (M = methyl; PW = produced water; AW = artificially weathered, UW = unweathered).

					Sheens Collected in the Field								Wave Tank (Sheen Formation)				
Sample ID		*SeaRose Crude Oil*	*PW AW*	*PW UW*	*SN1*	*SN2*	*SN3*	*SN4*	*SN5*	*SN6*	*SN7*	*SN8*	Time (minutes)				
													0	5	15	30	60
Compound		$ng \cdot g^{-1}$	$ng \cdot L^{-1}$	$ng \cdot L^{-1}$	$ng \cdot L^{-1}$								$ng \cdot L^{-1}$				
n-decane	C_{10}	4,325,746		16,830										155,689	273		
undecane	C_{11}	4,510,843	1,319	24,898										356,687	23,454	247	
dodecane	C_{12}	4,532,445	4,941	41,548										504,005	131,447	183	
tridecane	C_{13}	4,809,366	12,866	65,220										590,805	276,605	1,280	
tetradecane	C_{14}	5,334,918	23,213	92,100										723,716	392,772	9,288	
pentadecane	C_{15}	5,448,463	33,777	110,343		238	202							728,634	445,849	20,149	
hexadecane	C_{16}	4,046,824	37,628	106,039		433	1072		116					515,236	332,599	18,250	
heptadecane	C_{17}	4,748,408	53,977	120,077	145	902	2748		540					517,095	334,726	20,977	234
pristane		1,743,198	14,575	33,320		336	925	316	165					210,449	157,534	8,104	66
octadecane	C_{18}	3,852,173	48,084	98,876	191	1177	3950	117	893					455,469	286,617	20,231	187
phytane		1,828,247	21,888	40,478	141	416	1626	438	349					231,732	148,294	9,229	118
nonadecane	C_{19}	3,767,337	47,005	95,665	235	1446	4754	178	1201					425,468	287,922	19,862	201
eicosane	C_{20}	2,403,017	40,157	80,141	158	1081	4061	147	1159					317,824	184,021	12,950	200
heneicosane	C_{21}	2,567,567	41,761	81,828	136	1180	4405	178	1253					319,412	196,663	13,772	200
docosane	C_{22}	2,437,746	38,861	72,959	122	1142	4115	203	1185					308,361	186,525	13,047	187
tricosane	C_{23}	2,546,486	40,153	74,874	180	1221	4238	312	1235					344,424	195,092	13,476	261
tetracosane	C_{24}	2,471,112	37,967	65,723	185	1178	3943	348	1115					316,956	188,386	13,036	308
pentacosane	C_{25}	2,989,550	38,911	69,122		1189	4025	384	1178					374,156	218,955	15,090	290
hexacosane	C_{26}	3,358,546	42,727	67,303	102	1327	3919	462	1214					453,945	261,799	17,204	218
heptacosane	C_{27}	3,745,519	39,907	67,070	114	3088	3907	1188	1218					499,498	293,873	19,161	223
octacosane	C_{28}	5,718,564	43,081	66,408		2851	3766	1036	1192					826,224	464,055	28,745	157
n-nonacosane	C_{29}	4,144,394	47,916	60,368		2768	3353	1574	1160					596,964	329,303	20,052	178
tricontane	C_{30}	1,276,323	18,576	39,689		1261	2307	948	653					145,546	72,391	6,520	114

					Sheens Collected in the Field								Wave Tank (Sheen Formation)				
Sample ID		***SeaRose Crude Oil***	***PW AW***	***PW UW***	***SN1***	***SN2***	***SN3***	***SN4***	***SN5***	***SN6***	***SN7***	***SN8***	**Time (minutes)**				
													0	**5**	**15**	**30**	**60**
Compound		$ng \cdot g^{-1}$	$ng \cdot L^{-1}$	$ng \cdot L^{-1}$	$ng \cdot L^{-1}$								$ng \cdot L^{-1}$				
n-heneicontane	C_{31}	1,119,051	28,913	33,206		873	1978	598	594					135,466	68,863	5,546	113
dotriacontane	C_{32}	609,419	23,537	28,168		519	1492	482	413					83,922	43,637	2,902	0
tritriacontane	C_{33}	422,029	12,866	16,694		432	1097	393	401					65,599	32,157	2,021	
tetratriacontane	C_{34}	247,113	10,548	13,334		260	775	301	315					43,577	18,710	1,171	
n-pentatriacontane	C_{35}	128,149	7,033	10,885		222	677	248	348					25,668	9,838	515	
17β(H), 21α(H)-hopane		36,188	1,387	1,448				61						4,204	2,809	201	
naphthalene		1,128,773	23,321	274,759										94,967	8,504		
M-naphthalene		2,262,295	39,973	229,067										269,804	80,135	201	
di-M-naphthalene		2,570,303	34,196	114,436										375,172	161,192	1,762	
triM-naphthalene		1,684,616	20,227	45,058										268,062	128,694	3,831	
tetra-M-naphthalene		792,154	9,600	16,487										127,372	68,478	2,767	
acenaphthene		36,918	862	2,578										5,505	2,508		
acenaphthylene			353	1,920													
fluorene		134,872	5,597	13,748										21,027	10,998	310	
methylfluorene		256,121	6,896	12,746			153							39,575	21,791	948	
dimethylfluorene		264,791	6,663	8,967			198							42,178	23,066	1,185	
trimethylfluorene		183,241	4,643	6,377										35,083	18,584	1,042	
dibenzothiophene		32,392	1,582	2,825										6,124	3,091	119	
M-dibenzothiophene		88,342	2,662	2,863			109							15,270	8,236	374	
di-M-dibenzothiophene		101,337	2,554	3,252										17,905	9,645	462	
tri-M-dibenzothiophene		71,424	1,883	2,108										11,431	6,125	309	
tetra-M-dibenzothiophene		39,995	861	991										6,274	3,544	175	
phenanthrene		275,999	10,737	19,132										41,416	23,187	1,172	
anthracene		8,039					367		104					703	406		
M-phenanthrene		497,069	14,006	19,117		111	543		134					77,634	43,034	2,422	
di-M-phenanthrene		460,235	11,002	12,966			387	137						71,592	38,286	2,284	
tri-M-phenanthrene		296,174	6,817	7,589			207	105						45,737	24,490	1,459	
tetra-M-phenanthrene		146,368	3,315	4,144										23,862	11,659	698	
fluoranthene		7,307		414										909	601		

					Sheens Collected in the Field								Wave Tank (Sheen Formation)				
Sample ID		***SeaRose Crude Oil***	***PW AW***	***PW UW***	***SN1***	***SN2***	***SN3***	***SN4***	***SN5***	***SN6***	***SN7***	***SN8***	**Time (minutes)**				
													0	**5**	**15**	**30**	**60**
Compound		$ng \cdot g^{-1}$	$ng \cdot L^{-1}$	$ng \cdot L^{-1}$	$ng \cdot L^{-1}$								$ng \cdot L^{-1}$				
pyrene		12,122	376	512										1,912	883		
M-pyrene		85,827	2,075	2,436			132							11,650	7,100	432	
di-M-pyrene		114,253	2,685	2,767										17,222	9,080	529	
tri-M-pyrene		105,509	2,625	2,641			120							15,752	8,600	493	
tetra-M-pyrene		112,938	2,322	2,814			150							18,415	9,679	557	
naphthobenzothiophene		15,845	314	523										2,126	1,122		
M-naphthobenzothiophene		42,402	908	1,209			237	148						7,154	3,601	192	
di-M-NBenzothiophene		93,320	1,840	3,645										23,992	12,808	599	
tri-M-Nbenzothiophene		31,184	601	1,012										4,810	2,546	135	
tetra-M-Nbenzothiophene		19,313	403	605										2,856	1,587		
benz[*a*]anthracene		12,211	450	612										1,059	812		
chrysene		42,739	1,173	1,404			116							6,449	3,541	229	
M-chrysene		79,010	1,947	1,945			319		117					11,980	6,540	379	
di-M-chrysene		75,845	2,023	2,907			115							28,538	6,172	337	
tri-M-chrysene		58,712	1,441	1,466											4,512	239	
tetra-M-chrysene		50,074	1,130	1,200										7,391	3,826	195	
benzo[*b*]fluoranthene		17,818	245	818										1,973	1,206		
benzo[*k*]fluoranthene		6,532															
benzo[*e*]pyrene		17,000	290	710										2,040	1,193		
benzo[*a*]pyrene		5,301	210	397										422	323		
perylene																	
indeno[1,2,3-*cd*]pyrene																	
dibenz[*a,h*]anthracene		20,187												1,181	1,038		
benzo[*ghi*]perylene		14,583	610	787										1,082	827		